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2,4,4,6-Tetrabromo-2,5-cyclohexadienone (TABCO) as a Versatile, Efficient, and Chemoselective Catalyst for the Acetalization and Transacetalization of Carbonyl Compounds, the Preparation of Acetonides from Epoxides and Acylals (1,1-Diacetates) from Aldehydes

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The efficient and chemoselective preparation of acetals and ketals from carbonyl compounds, transacetalization reactions, the conversion of epoxides to acetonides, and the preparation of acylals from aldehydes in the presence of catalytic amounts of 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TABCO) are described.

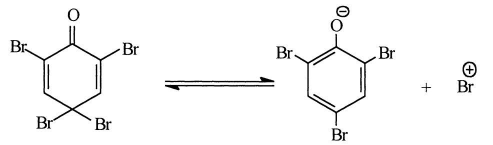
The protection of functional groups in the process of the total synthesis of complex organic molecules is an almost inevitable reaction.[1] Acetals are one of the most widely used protecting groups for carbonyl compounds. Acetals are generally stable to bases, Grignard reagents, alkyllithium reagents, metal hydrides, Na/NH_3, Witting reagents, hydrogenation reactions, oxidants, bromination, and esterification reagents.[1,2] This stability towards a wide range of reagents and reaction conditions has revealed the importance of these derivatives of carbonyl compounds in organic synthesis.[1,2] In addition, chiral acetals are particularly important precursors for preparing enantiomerically pure compounds.[3] Numerous methods reported in the literature for acetalizations include the use of protic acids,[4] Lewis acids,[5] ion-exchange resins,[6] rhodium complexes,[7] and transition metals, such as rhodium, iridium, palladium, and platinum supported on carbon.[8] It has been shown that the use of Lewis acids in these transformations offers several advantages over conventional protic acid methods.[9] Among the acetals, open-chain acetals have frequently been subjected to special attention owing to their liability as compared with cyclic *O*,*O*-acetals.[2] Acyclic acetals are usually only used when selective or very mild deprotection conditions are required.[10] The open-chain acetals are almost less easily formed than cyclic analogues. Therefore, their preparation generally requires more effective conditions compared with the cyclic acetals.[11] Acetalization reaction is generally accepted to proceed through the formation of the corresponding hemiacetal, and then another alkoxy unit derived from the alcohol replaces the hydroxy function of the hemiacetal. Each step is reversible, and the entire sequence, starting from the carbonyl compound and ending with acetal, is an equilibrium process.[12] The main problem in the acetal formation is to shift the equilibrium to the acetal formation by reducing the amount of water produced in the equilibrium system. In the preparation of dialkyl acetals, the use of trialkyl orthoformates (for example, triethyl orthoformate [$(EtO)_3CH$] in the presence of anhydrous $FeCl_3$,[13] dry HCl,[14] Amberlyst-15,[15] WCl_6,[16] $ZrCl_4$,[17] and so on as catalysts in absolute ethanol) could be one way to circumvent this problem. The water formed in the acetalization reaction reacts immediately with the orthoformate (for example, triethyl orthoformate) and produces alcohol (ethanol) and an ester (ethyl formate), with consequence to shift the equilibrium towards diethyl acetal formation.[18] The role of the orthoformate is not limited only to the reaction with water, but it also takes part in the acetalization reaction, itself.[19] The removal of water by continuous azeotropic distillation in benzene is undoubtedly one of the most commonly used methods for this purpose. In some cases, dehydrating agents, such as $CaSO_4$,[20] Al_2O_3,[21] $CuSO_4$,[22] molecular sieves,[23] and $MgSO_4$,[24] are also used to adsorb water.

A literature survey shows that more attention has been paid to the development of new methods for the generation of cyclic acetals (1,3-dioxolanes, 1,3-dioxanes) in comparison with the open-chain ones. This is due to the higher stability of cyclic acetals than their open-chain analogs.[1,12] It is worth mentioning that aldehydes are generally more reactive than ketones in acetalization reactions.[25]

However, traditional acid catalyzed acetalization methods have not always given satisfactory results, especially when the substrate suffers from acid and/or heat sensitivity. Catalysts such as chlorotrimethylsilane (TMSCl)[26] and trimethylsilyl triflate (TMSOTf),[27] can be used effectively for acetalization reactions under mild reaction conditions. Very recently, Yamamoto et al. found that scandium(III) trifluoromethanesulfonimide (Triflimide) [$Sc(NTf)_3$] is a suitable catalyst for preparing not only acyclic acetals, but also cyclic acetals. Using this method, cyclic acetals were obtained by an in situ acetal-exchange reaction of ketones, diols, and trimethyl orthoformate in the presence of $Sc(NTf)_3$ as a catalyst under very mild reaction conditions. This method is the first example of preparing cyclic acetals by an in-situ transacetalization reaction.[28]

Results and Discussion

The bromination of phenol produces a highly crystalline

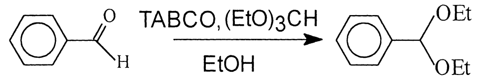


(I)

2,4,4,6-Tetrabromo-2,5-cyclohexadienone

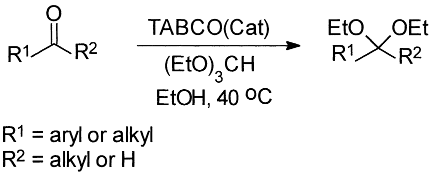
Scheme 1.

Table 1. Optimization of Reaction Conditions for the Conversion of Benzaldehyde to Benzaldehyde Diethyl Acetal



Sub/(EtO)$_3$CH/EtOH/TABCO	Time	Yield%[a)]
1/0/10/0.1, RT	24 h	6
1/3/0/0.1, RT	24 h	68
1/3/5/0.1, RT	55 min	85
1/3/5/0.1, 60 °C	5 min	98
1/3/5/0.1, 50 °C	5 min	98
1/3/5/0.1, 40 °C	10 min	98
1/3/5/0.2, 40 °C	5 min	98

a) Yields based on GC yield using *n*-heptane as internal standard.



Scheme 2.

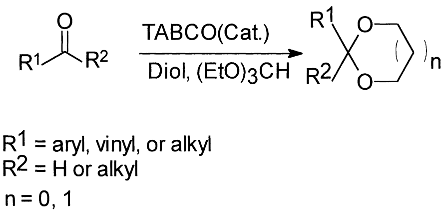
compound, 2,4,4,6-tetrabromo-2,5-cyclohexadienone (I, TABCO).[29] This *tetrarbromo* derivative of phenol (I) carries a strong electrophilic bromine species that can be used as a non-traditional Lewis acid for the catalysis of different reactions (Scheme 1).

Now, we report on the use of this compound as a catalyst for the acetalization and transacetalization of carbonyl compounds as well as the preparation of acetonides from epoxides and acylals (1,1-diacetates) from aldehydes.

In order to optimize the reaction conditions, first the reaction of benzaldehyde with (EtO)$_3$CH and TABCO in ethanol at different temperatures was studied. We found that TABCO (0.1 equiv) efficiently catalyzes the diethyl acetalization of benzaldehyde with (EtO)$_3$CH (3 equiv) in ethanol (5 equiv) at 40 °C in 10 min. The results of this reaction under different reaction conditions are given in Table 1.

We therefore used the optimized conditions for diethyl acetalization reactions of different carbonyl compounds (Scheme 2).

Different types of aldehydes including benzaldehyde derivatives, aliphatic-, and α,β-unsaturated aldehydes were converted to their corresponding diethyl acetals with TABCO (0.1 mmol) at 40 °C in high-to-excellent yields (Table 2, entries 1–10). Cyclic aliphatic ketones, such as cyclohexanone (Table 2, entry 15), undergo acetalization reactions much faster with higher efficiency than the open-chain ketones, such as acetophenone, benzyl methyl ketone, and benzyl ethyl ketone (Table 2, entries 11, 18, 19). This observation clearly shows that the overall acetalization reactions are more strongly affected by the steric factors compared to electronic.



Scheme 3.

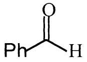
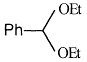
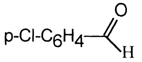
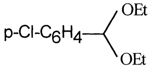
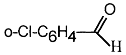
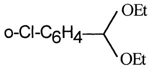
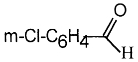
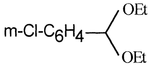
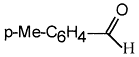
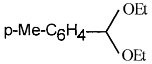
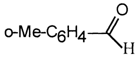
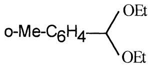
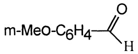
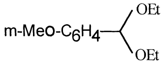
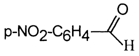
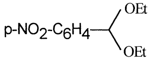
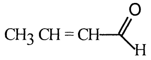
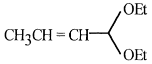
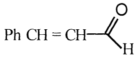
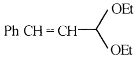
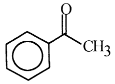
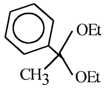
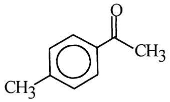
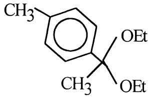
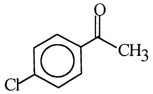
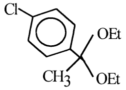
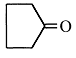
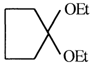
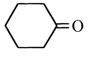
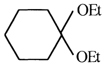
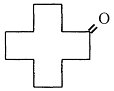
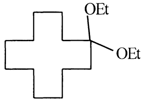
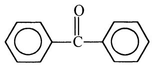
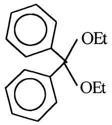
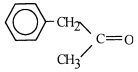
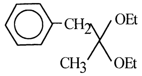
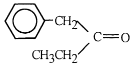
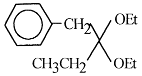
The results given in Table 2 show that based on the different reactivity of aldehydes and ketones in these reactions, a chemoselective protection of carbonyl groups can be achieved by this method. In this regard, as illustrated in Table 3, bezaldehyde was protected in the presence of acetophenone with a ratio of 98/2% and in the presence of benzophenone with a ratio of 100/0%. Thus, by this method, aldehydes were selectively protected as their diethyl acetals in the presence of ketones.

Recently, Sc(NTf)$_3$, Sc(OTf)$_3$,[28] and WCl$_6$[16a] have been employed as powerful catalysts for the in situ transacetalization of carbonyl compounds in the presence of trimethyl orthoformate and a diol. These are leading reports on the use of Lewis acid catalysts for the in situ transacetalization of carbonyl compounds and also for the preparation of 1,3-dioxanes under mild reaction conditions. These reports prompted us to investigate the capability of TABCO to conduct similar transformations. Along this line, we found that the 1,3-dioxanation of a variety of structurally different carbonyl compounds could be achieved in the presence of 1,3-propanediol (2 equiv), (EtO)$_3$CH (3 equiv), and TABCO as a catalyst in-high-to excellent yields at room temperature in dry ethanol (Scheme 3, Table 4).

In all of the reactions in our studies for the preparation of 1,3-dioxane and 1,3-dioxolane, transient formations of diethyl acetals were detected by GC analysis of the reaction mixtures, which, in turn, were smoothly converted to their corresponding 1,3-dioxanes and 1,3-dioxolanes during the progress of the reaction. On the other hand, the 1,3-dioxanation of benzaldehyde with 1,3-propanediol (2 equiv) and TABCO (0.2 equiv) in the absence of (EtO)$_3$CH was not successful, even after 20 h. However, the transacetalization of benzaldehyde diethyl acetal under similar reaction conditions was achieved in an excellent yield within 3 min. (Table 4, entry 1). This observation strongly indicates the necessity of the in situ generation of the diethyl acetal, followed by its transacetalization to the corresponding 1,3-dioxane or 1,3-dioxolane in the reaction mixture (Scheme 4).

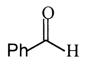
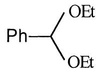
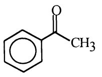
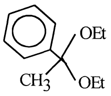
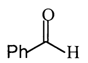
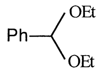
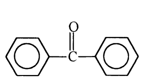
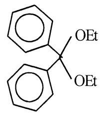
We have applied this method to the generation of 1,3-dioxanes and 1,3-dioxolanes from various types of carbonyl compounds using 1,3-propanediol and 1,2-ethanediol, respectively, in the presence of ethyl orthoformate, and also a catalytic amount of TABCO (Table 4).

Table 2. Diethyl Acetalization of Aldehydes and Ketones with TABCO as a Catalyst and $(EtO)_3CH$ (3 equiv) in EtOH (5 equiv) at 40 °C

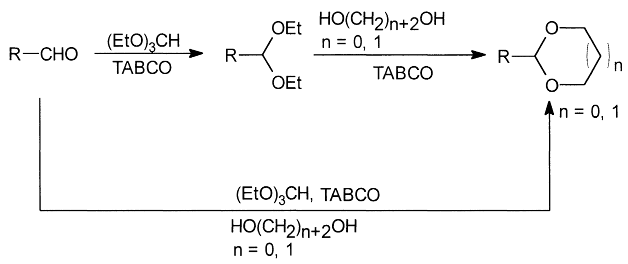
Entry	Substrate	Product[a)]	Sub/Catalyst	Time/min	Yield[b)]/%
1	 PhCHO	 PhCH(OEt)_2	1/0.1	10	98
2	 $p\text{-Cl-C}_6\text{H}_4\text{-CHO}$	 $p\text{-Cl-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	20	90
3	 $o\text{-Cl-C}_6\text{H}_4\text{-CHO}$	 $o\text{-Cl-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	15	91
4	 $m\text{-Cl-C}_6\text{H}_4\text{-CHO}$	 $m\text{-Cl-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	10	94
5	 $p\text{-Me-C}_6\text{H}_4\text{-CHO}$	 $p\text{-Me-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	5	96
6	 $o\text{-Me-C}_6\text{H}_4\text{-CHO}$	 $o\text{-Me-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	12	94
7	 $m\text{-MeO-C}_6\text{H}_4\text{-CHO}$	 $m\text{-MeO-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	15	92
8	 $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$	 $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH(OEt)}_2$	1/0.1	35	90
9	 $\text{CH}_3\text{CH=CH-CHO}$	 $\text{CH}_3\text{CH=CH-CH(OEt)}_2$	1/0.1	10	94
10	 PhCH=CH-CHO	 PhCH=CH-CH(OEt)_2	1/0.1	15	91
11			1/0.3	85	90
12			1/0.3	70	88
13			1/0.3	140	91
14			1/0.2	30	90
15			1/0.2	25	92
16			1/0.2	40	89
17			1/0.5	180	60
18			1/0.3	75	87
19			1/0.3	80	85

a) All the products were known compounds and were identified by comparisons of their spectral data (IR, NMR and MS) with known samples.[2,14–15,17] b) Isolated yield.

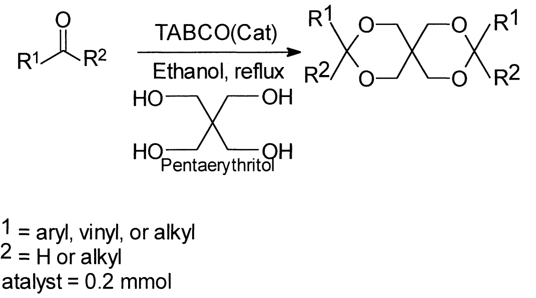
Table 3. Selective Diethyl Acetalization with TABCO as a Catalyst and $(EtO)_3CH$ (3 equiv) in EtOH (5 equiv) at 40 °C

Entry	Substrate 1 Substrate 2	Product 1 Product 2	Sub. 1/Sub. 2/TABCO	Time/min	Yield[a]/%
1			1/1/0.1	30	98
					2
2			1/1/0.2	60	100
					0

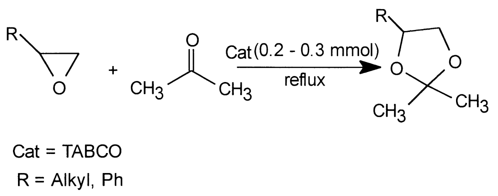
a) Yields based on GC and NMR analysis.



Scheme 4.



Scheme 5.



Scheme 6.

The chemoselectivity of the method is shown by competitive reactions between benzaldehyde and acetophenone or cyclohexanone, and also between cyclohexanone and 4-phenyl-2-butanone. As it is evident from the results tabulated in Table 5, the method can be successfully used for chemoselective reactions of different carbonyl compounds.

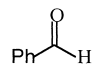
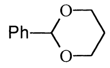
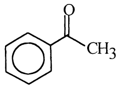
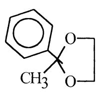
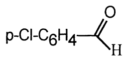
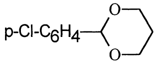
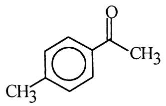
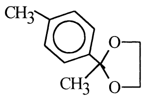
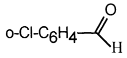
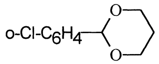
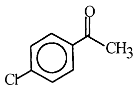
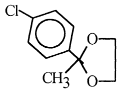
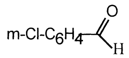
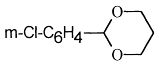
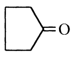
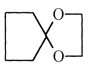
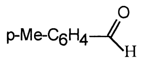
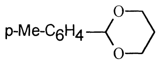
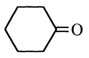
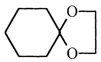
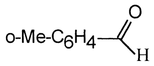
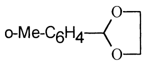
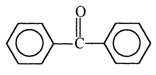
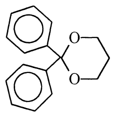
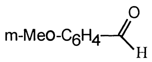
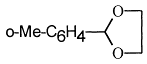
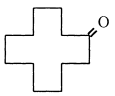
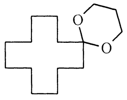
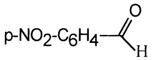
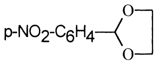
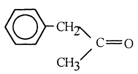
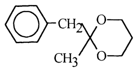
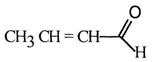
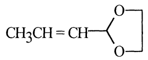
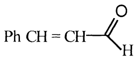
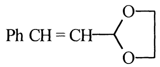
We also studied the reaction of benzaldehyde with various diols in the presence of TABCO and $(EtO)_3CH$ in dry EtOH at 50 °C. The results are given in Table 6. We observed that 3-hexyne-2,5-diol with a linear structure can not give the desired cyclic acetal. If we compare the rate of the reaction of benzaldehyde with 1,3-propandiol and 1,3-butandiol, we observe that the later diol in a faster reaction produces a higher yield of the corresponding cyclic acetal than of 1,3-propandiol (Table 6, entries 1,5). The reaction of benzaldehyde with other diols shows that the formations of large cyclic acetals are more difficult and require more time and depend on the geometrical shape of the diol.

2,2-Bis(hydroxymethyl)-1,3-propanol acetal can be used as a potential protective group for aldehydes and ketones as well as important derivatives of carbonyl compounds, since most of them are crystalline substances and have sharp melting points.[30] Therefore, the synthesis of diacetals from pentaerythritol with aldehydes and ketones in the presence of TABCO in refluxing dry ethanol was studied (Scheme 5).

As shown in Table 7, various types of aldehydes and ketones in the presence of a catalytic amount of TABCO reacted with pentaerythritol in refluxing dry ethanol to give the corresponding diacetals in good-to-excellent yields. Hindered ketones, such as acetophenone and benzophenone, remained almost intact, or gave a low yield.

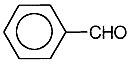
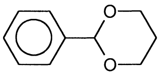
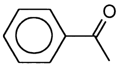
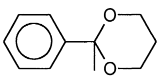
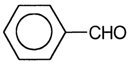
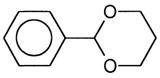
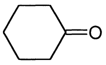
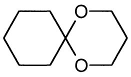
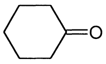
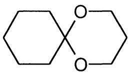
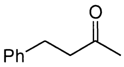
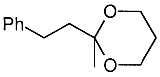
An acetalization reaction between acetone and 1,2-diols produces 1,3-dioxolanes, which are also called acetonides. Acetonide derivatives are useful protected synthetic intermediates, particularly in carbohydrate and steroid chemistry.[12a,31] Acetonides can be easily prepared in two ways: a) by the hydrolysis of epoxides to the appropriate diols, followed by an acetalization reaction in the presence of acetone and a Lewis acid, and b) by the direct condensation of epoxides with acetone and Lewis acids as catalysts. Some Lewis acids, such as $BF_3{\cdot}Et_2O$,[31] $CuSO_4$,[31a] and anhydrous $RuCl_3$[32] in acetone, have been used to convert epoxides to their corresponding acetonides. We have used TABCO as a catalyst for preparing ace-

Table 4. Acetalization of Aldehydes and Ketones with TABCO as a Catalyst and $(EtO)_3CH$ (3 equiv), 1,3-Propanediol or 1,2-Ethanediol (2 equiv) in Dry EtOH (2 mL) at 50 °C

Entry	Substrate	Product[a)]	Sub/Catalyst	Time/h	Yield[b)]/%	Entry	Substrate	Product[a)]	Sub/Catalyst	Time/h	Yield[b)]/%
1			1/0.2	3	92	11			1/0.3	50	75
2			1/0.2	4	94	12			1/0.3	40	85
3			1/0.2	4	91	13			1/0.3	25	89
4			1/0.2	3	95	14			1/0.3	15	90
5			1/0.2	3	87	15			1/0.3	20	89
6			1/0.1	6	85	16			1/0.5	180	20
7			1/0.2	7	90	17			1/0.3	50	87
8			1/0.2	6	94	18			1/0.3	65	89
9			1/0.2	6	91						
10			1/0.3	45	80						

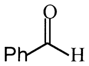
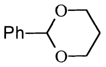
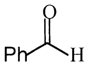
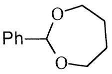
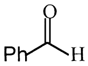
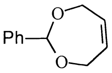
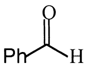
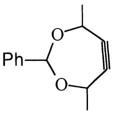
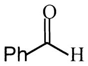
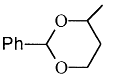
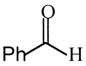
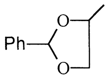
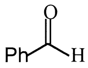
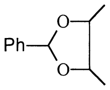
a) All the products were known compounds and were identified by comparisons of their spectral data (IR, NMR and MS) with known samples.[2,16] b) Isolated yield.

Table 5. Selective Acetalization of Carbonyl Compounds in the Presence of $(EtO)_3CH$ and TABCO in Dry EtOH (2 mL) at 50 °C

Entry	Substrate	Product	Sub. 1/Sub. 2/Diol/ $(EtO)_3CH$/TABCO	Time/h	Yield[a)]/%
1			1/1/2/3/0. 2	4	96
					4
2			1/1/2/3/0. 2	5	94
					6
3			1/1/2/3/0. 2	25	100
					0

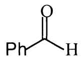
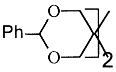
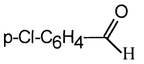
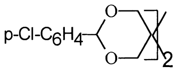
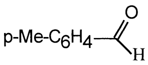
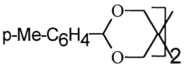
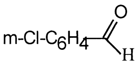
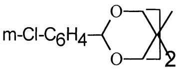
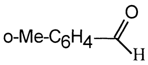
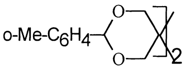
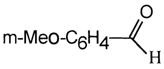
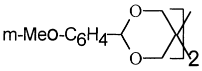
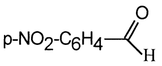
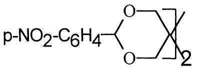
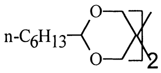
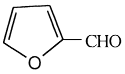
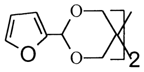
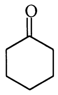
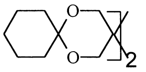
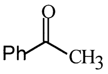
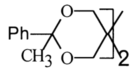
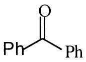
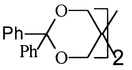
a) Yields based on GC and NMR analysis.

Table 6. Acetalization of Benzaldehyde with Different Diols (2 equiv) and $(OEt)_3CH$ (3 equiv), Catalyzed with TABCO in EtOH (2 mL) at 50 °C

Entry	Substrate	Product	Sub./Catalyst	Time/h	Yield[a)]/%
1			1/0.2	3	92
2			1/0.2	6	73
3			1/0.2	7	56
4			1/0.2	15	0
5			1/0.2	2.5	97
6			1/0.2	4.5	92
7			1/0.2	5	90

a) Isolated yield.

Table 7. Acetalization of Carbonyl Compounds with Pentaerythritol using TABCO (0.2 mmol) as Catalyst in Dry EtOH under Reflux Conditions

Entry	Substrate	Product[a)]	Time/h	Yield[b)]/%
1			1.5	90
2			2	92
3			2	92
4			0.8	92
5			1.2	94
6			4.2	89
7			3	90
8	n-C_6H_{13}CHO		0.7	94
9			1.8	94
10			20	90
11			24	35
12			24	0

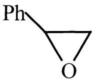
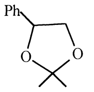
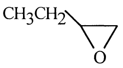
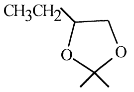
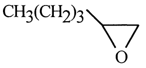
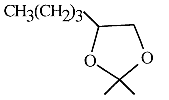
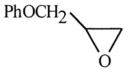
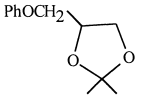
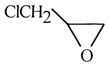
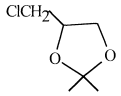
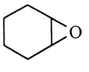
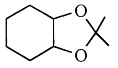
a) All the products were known compounds and were identified by comparisons of their spectral data (IR, NMR and MS) with known samples.[30] b) Isolated yield.

tonides from epoxides (Scheme 6).

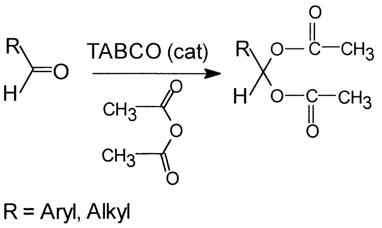
Different epoxides were reacted with acetone in the presence of TABCO, and gave the desired products in excellent yields (90–94% yield). Among the epoxides which we have used for this study, only epichlorohydrine (Table 8, entry 5) produced its corresponding acetonide in only 22% yield.

1,1-Diacetates (acylals) are useful protective groups for aldehydes.[1] The relative acid stability of 1,1-diacetates compared to the corresponding O,O-acetals is an interesting feature of such 1,1-diacetates as carbonyl groups derivatives.[1] The reaction of aldehydes with acetic anhydride in the presence of a Lewis acid is the most common procedure for the preparing acylals. Different Lewis acid catalysts and strong protic acids, such as H_2SO_4,[33a] H_3PO_4, and CH_3SO_3H,[33b] have been reported for this conversion. However, the yields of the reaction are low because under these conditions, deprotection

Table 8. Conversion of Epoxides to 1,3-Dioxolanes Catalyzed with TABCO in Acetone under Reflux Conditions

Entry	Substrate	Product[a)]	Sub./Catalyst TABCO	Time/(min), [h]	Yield[b)]/%
1			1/0.2	(20)	94
2			1/0.2	[12]	95
3			1/0.2	[24]	90
4			1/0.3	[15]	94
5			1/0.3	[24]	22
6			1/0.2	[2.5]	94

a) All the products were known compounds and were identified by comparisons of their spectral data (IR, NMR and MS) with known samples.[31–32] b) Isolated yield.



Scheme 7.

of acylals can be also occurred easily. Lewis acids such as $ZnCl_2$,[34a] $FeCl_3$,[34b] PCl_3,[34c] I_2,[34d] $Sc(OTf)_3$,[34e] and solid acidic materials like Nafion-H,[34f] zeolites,[34g] expansive graphite,[34h] and clay[34i] have also been used. We observed that TABCO could act as an effective catalyst for the preparation of acylals from their corresponding aldehydes. Various types of aromatic aldehydes, bearing either electron-withdrawing or electron-releasing groups and aliphatic aldehydes, were converted to their corresponding acylals in the presence of acetic anhydride and TABCO in good-to-excellent yields (Scheme 7, Table 9).

By this method, similar to other reported methods in the literature, the preparation of 1,1-diacetates from ketones can not occur.[34] A plausible explanation for the role of TABCO in this reaction is that TABCO could act as a source of electrophilic bromine which, in turn, activates the carbonyl group as well as acetic anhydride for this reaction.

Conclusion

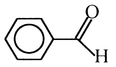
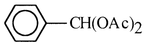
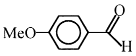
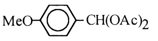
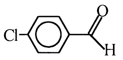
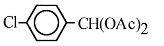
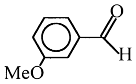
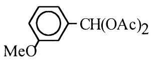
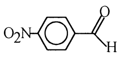
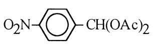
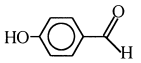
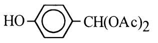
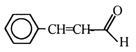
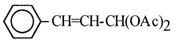
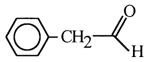
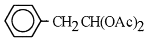
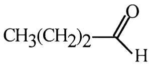
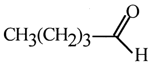
The catalytic nature of the method, easy work-up, high chemoselectivity of the method, and high yields of the products, are worth mentioning as advantages of the presented method.

Experimental

General: All chemicals, were either prepared in our laboratories or were purchased from Fluka and Merck Companies. Because the products are known compounds, the elemental analyses are not given in the text. The products were identified by comparing their mp, IR, NMR, and mass spectra with those reported for authentic samples. Progress of the reactions was followed by TLC using TLC-Cards Silica-gel having fluorescent indicator 254 nm or by GC using a Shimadzu gas chromatograph GC-14A, equipped with a flame ionization detector and a 3-meter length glass column packed with a DC-240 stationary phase and nitrogen as the carrier gas. Infrared spectra were recorded on a Perkin Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument.

General Procedure for the Acetalization of Carbonyl Compounds to Diethyl Acetals Catalyzed with TABCO in the Presence of Triethyl Orthoformate and Absolute Ethanol: To a mixture of aldehydes or ketones (1.0 mmol), absolute ethanol (5 mmol), and triethyl orthoformate (3 mmol), TABCO (Table 2) was added; the resulting solution was stirred at 40 °C, and the progress of the reaction was monitored by TLC or GC. After completion of the reaction, a cold aqueous solution of NaOH (10%, 25 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic extracts were washed with water (25 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure product(s). Further purification was performed by vacuum distillation to afford pure diethyl acetal

Table 9. Preparation of Acylals from Aldehydes in the Presence of Acetic Anhydride Catalyzed by TABCO at 50 °C

Entry	Substrate	Products[a)]	Sub/Catalyst	Time/h	Yield[b)]/%
1			1/0.2	4	92
2			1/0.3	18	85
3			1/0.2	7	94
4			1/0.3	19	94
5			1/0.4	6	80
6			1/0.4	25	87
7			1/0.3	36	82
8			1/0.2	7	90
9		$CH_3(CH_2)_2CH(OAc)_2$	1/0.1	15	94
10		$CH_3(CH_2)_3CH(OAc)_2$	1/0.1	20	94

a) All the products were known compounds and were identified by comparisons of their spectral data (IR, NMR and MS) with known samples.[33–34] b) Isolated yield.

in good-to-excellent yields (Table 2). All of the products were known compounds, and were identified by comparisons of their spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS) with those reported in the literature.[2,14–15,17] Selected spectral data for:

Benzaldehyde Diethyl Acetal:[14–15] ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.18–1.27 (m, 6H), 3.42–3.58 (m, 4H), 5.48 (s, 1H), 7.24–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 15.17, 60.21, 100.87, 126.59, 127.84, 128.11, 138.92.

4-Chlorobenzaldehyde Diethyl Acetal:[14–15] ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.02 (m, 5H), 5.14 (s, 1H), 3.12 (q, 4H), 0.91 (t, 6H). ^{13}C NMR ($CDCl_3$, 63 MHz) δ 137.5, 133.9, 128.2, 128.1, 100.6, 60.8, 15.1.

Acetophenone Diethyl Acetal:[14–15,17] ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.90 (dd, 2H), 7.22 (m, 3H), 3.53 (m, 4H), 1.63 (s, 3H), 1.24 (t, 6H) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz) δ 151.5, 135.6, 135.0, 133.8, 108.8, 64.3, 34.8, 23.1, 22.6.

General Procedure for In-Situ Transacetalization of Carbonyl Compounds to 1,3-Dioxanes and 1,3-Dioxolanes Catalyzed with TABCO: To a solution of carbonyl compounds (1.0 mmol), 1,3-propanediol or 1,2-ethanediol (2 mmol), and $(EtO)_3CH$ (3 mmol) in dry ethanol (2 mL), TABCO (Table 4) was added; the resulting solution was stirred vigorously at 50 °C. The progress of the reaction was monitored by TLC or GC. After completion, the reaction was quenched with a cooled aqueous solution of NaOH (10%, 25 mL) and the organic layer was separated and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were washed with water (2 × 25 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure 1,3-dioxane(s) and 1,3-dioxolane(s). Further purification was achieved by vacuum distillation to give pure product(s) in good-to-excellent yield(s) (Table 4). All of the products were known compounds and were identified by a comparison of their spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS) with those reported in the literature.[2,16] Selected spectral data for:

2-Phenyl-1,3-dioxane:[16] ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.37–1.44 (m, 1H), 2.18–2.27 (m, 1H), 3.92–4.02 (m, 2H), 4.24–4.30 (m, 2H), 5.51 (s, 1H), 7.33–7.43 (m, 3H), 7.51–7.54 (m, 2H).

2-(4-Nitrophenyl)-1,3-dioxane:[16] ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.44–1.50 (m, 1H), 2.14–2.26 (m, 1H), 3.94–4.04 (m, 2H), 4.24–4.51 (m, 2H), 5.55 (s, 1H), 7.62–7.66 (m, 2H), 7.98–

8.29 (m, 2H).

General Procedure for the Synthesis of Cyclic Diacetals by Condensation of 2,2-Bis(hydroxymethyl)-1,3-propandiol with Carbonyl Compounds Catalyzed by TABCO: A mixture of carbonyl compounds (2.0 mmol), 2,2-bis(hydroxymethyl)-1,3-propandiol (pentaerythritol) (1.2 mmol), and TABCO (Table 7) as a catalyst in dry ethanol (10 mL) was stirred at refluxing temperature using a Dean–Stark apparatus for water removal. The progress of the reaction was monitored by TLC and GC. After completion, the mixture was cooled and then NaOH (5%, 25 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed with water (2 × 20 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure provided a crude product. The crude product was purified by silica-gel column chromatography (petroleum ether 60–80 °C/$CHCl_3$, 8/2) to afford pure crystals of their corresponding diacetals in good-to-excellent yields. The crude product could also be purified by recrystallization in alcohols such as ethanol, butanol, and isopropyl alcohol to give pure crystalline diacetals (Table 7). All of the products were known compounds, and were identified by comparisons of their spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS) with those reported in the literature.[30] Selected spectral data for some cyclic diacetals with the following aldehydes:[30]

Benzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.70–7.42 (m, 10H), 5.01 (d, 2H), 4.34 (s, 2H), 4.01–3.52 (m, 6H). IR 2960, 2925, 1600, 1175, 745, 965 cm^{-1}.

4-Methylbenzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.30–7.12 (m, 8H), 5.42 (s, 2H), 4.85 (d, 2H), 3.81–3.72 (m, 4H), 3.60 (d, 2H), 2.34 (s, 6H). IR 2910, 2862, 1600, 1460, 1390, 1050, 805 cm^{-1}.

4-Chlorobenzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.61–7.02 (dd, 8H), 4.55 (d, 2H), 4.33 (s, 2H), 3.61–3.23 (m, 6H). IR(neat) 2960, 2930, 1600, 1500, 1090, 820 cm^{-1}.

Furfural: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.61–7.42 (m, 6H), 4.90 (d, 2H), 4.24 (s, 2H), 3.61–3.22 (m, 6H). IR(neat) 2960, 2940, 2850, 1090, 740 cm^{-1}.

Direct Conversion of Epoxides to 1,3-Dioxolanes Catalyzed with TABCO in Dry Acetone under Reflux Conditions: To a solution of epoxide (1.0 mmol) in dry acetone (5 mL), appropriate amounts TABCO (Table 8) were added, and the resulting solution was stirred under the reflux condition. The progress of the reaction was monitored by TLC or GC. After completion (Table 8), the reaction was quenched with a cold aqueous solution of NaOH (5%, 20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were washed with water (2 × 20 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure 1,3-dioxolanes. Further purification was achieved by vacuum distillation to give pure product(s) in-good-to excellent yield(s) (Table 8). All of the products were known compounds, and were identified by comparisons of their spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS) with those reported in the literature.[31–32] Selected spectral data for:

2,2-Dimethyl-4-phenyl-1,3-dioxolane:[31–32] (Table 8, Entry 1): ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.10 (s, 5H), 4.85 (dd, 1H), 4.12 (dd, 1H), 3.45 (dd, 1H), 1.43 (s, 3H), 1.38 (s, 3H). IR (neat) 3040, 2990, 3880, 1500, 1450, 1370, 1220, 1160, 1070, 950, 860, 790, 700 cm^{-1}.

General Procedure for the Preparation of Acylals (1,1-Diacetate) from Aldehydes Catalyzed with TABCO in the Presence of Acetic Anhydride: To a magnetically stirred solution of aldehydes (1.0 mmol) and freshly distilled AC_2O (2mL), TABCO (Table 9) was added at 50 °C. The progress of the reaction was monitored by TLC or GC. After completion, the reaction was quenched with cold water (10 mL), and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The organic layer was separated and washed with saturated $NaHCO_3$ (2 × 25mL) and water 15 mL and then dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave the most pure acylals (1,1-diacetate). Further purification by column chromatography on silica gel using petroleum ether 60–80 °C/EtOAc as eluent afforded the desired product(s) in good-to-excellent yield(s) (Table 9). All of the products were known compounds and were identified by comparisons of their spectral data (IR, ^{1}H NMR, ^{13}C NMR, and MS) with those reported in the literature.[33–34] Selected spectral data for some acylals of the following aldehydes:[33–34]

Benzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.67 (s, 1H), 7.40 (s, 5H), 2.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 63 MHz), δ 168.1, 135.4, 129.3, 128.2, 126.2, 89.5, 20.1. IR (nujol) 1750, 1380, 1245, 1210, 1065, 1015, 960, 758, 695 cm^{-1}.

4-Nitrobenzaldehyde ^{1}H NMR ($CDCl_3$, 250 MHz), δ 8.05 (d, 2H), 7.47 (d, 2H), 7.45 (s, 1H), 2.10 (s, 6H). IR (nujol) 1760,1540, 1460, 1236, 1095, 1060 cm^{-1}.

4-Chlorobenzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.50 (s, 1H), 7.31 (s, 4H), 2.12 (s, 6H). IR (nujol) 1755, 1605, 1495, 1375, 1215 cm^{-1}.

4-Methoxybenzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.42 (s, 1H), 7.35 (d, 2H), 6.75 (d, 2H), 3.81 (s, 3H), 2.13 (s, 6H). IR (nujol) 1763, 1614, 1519, 1372, 1241, 1204 cm^{-1}.

Butyraldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 6.51 (m, 1H), 2.40–2.20 (m, 2H), 2.01 (s, 6H), 1.90–1.30 (m, 2H), 1.02 (t, 3H). IR (nujol) 2960, 1765,1374, 1244, 1208, 1010 cm^{-1}.

Cinnamaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.60–7.10 (m, 6H), 6.87 (d, 1H), 5.93 (dd, 1H), 2.10 (s, 6H). ^{13}C NMR ($CDCl_3$, 63 MHz), δ 168.2, 136.4, 135.3,128.8, 127.6, 127.0, 121.8, 89.7, 20.8. IR (nujol) 1755, 1660, 1490, 1470, 1245, 1195, 1120, 1060, 1005,940, 748, 690 cm^{-1}.

4-Methylbenzaldehyde: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.31 (q, 4H), 2.35 (s, 3H), 2.10 (s, 6H). ^{13}C NMR ($CDCl_3$, 63 MHz), δ 168.6, 139.6, 132.8, 129.2, 126.6, 89.8, 21.1, 20.7. IR (nujol) 1765, 1750, 1230, 1205, 1070, 1005, 960, 930, 815 cm^{-1}.

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